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Technical Progress Report 71-2—Semiannual
March 1 to August 31, 1971

SENSITIVITY FUNDAMENTALS

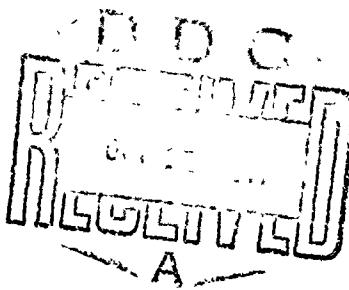
By: P. S. DeCARLI, D. S. ROSS, R. SHAW, and R. W. WOOLFOLK

Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
ARLINGTON, VIRGINIA

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PREFACE

This project is the responsibility of the Chemistry Laboratory's Physical Organic Chemistry Group in the Physical Sciences Division of Stanford Research Institute. Project organization and principal contributors to the technical work are:

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| Kinetics and Mechanisms of Thermal Decomposition: | D. S. Ross L. W. Pisziewicz P. De Carli |

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| 13. ABSTRACT <p>This report summarizes a six-month period of research on the relationship between detonation phenomena, chemical structure, and kinetics for isomeric dinitropropanes and other nitroalkanes, sponsored by the Office of Naval Research. Research on dinitropropanes is being carried out in three areas: high velocity detonation (HVD), low velocity detonation (LVD), and kinetics of thermal decomposition.</p> <p>Shock temperature calculations were made for seven nitroalkanes and nitrate esters over a range of 0 to 200 kbars. Smooth shock reaction times, measured at ambient temperatures and pressures, indicated that 1,1-DNE initiates faster than 1,1-DNP; methyl nitrite did not initiate at 45 kbar.</p> <p>Energy release under LVD conditions was calculated for EN, 1,1-DNP, NM and 1,1-DNE using TIGER code. Results indicate that 1,1-DNE has a greater energy release than 1,1-DNP with lower energy release than 1,1-DNP does undergo LVD; 1,1-DNP does not.</p> <p>Kinetic parameters for five nitro and dinitropropanes were measured in a modified VLPP apparatus. The two nongeminate nitroalkanes eliminate HONO with E_a at 39-41 kcal/mole, while three geminate dinitroalkanes decompose by C-N bond scission with E_a of 47 kcal/mole.</p> <p>Vibrationally excited 1,2-DP loses HF to form imonitrile at 135° with $k = 10^{13.5-49/\theta} \text{ sec}^{-1}$.</p> | | |

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SUMMARY

Physics and Chemistry of Detonation

Shock temperatures were calculated using the C_v and $C_v(T)$ models for some dinitroalkanes and alkyl nitrates for shock pressures in the range 0 to 200 kbar. Typical results at 100 kbar for the C_v model are: compound, temperature in °K; NM, 1318 (NM was run as a consistency check); 1,1-DNE, 1019; 1,1-DNP, 1008; 1,1,i-FDNP, 1198; 1,2-DNP, 956; EN, 1125; and NG, 962.

We have begun smooth shock reaction experiments with 1,1-DNP and 1,1-DNP at ambient preshock temperature and pressure. Preliminary results indicate that 1,1-DNE initiates faster than 1,1-DNP at the same shock pressure. Liquid methyl nitrite at ambient preshock temperature and 10 atmospheres preshock pressure did not initiate at a shock pressure of 45 kbar.

The static high pressure work and a study on the elimination of HF from vibrationally excited 1,2-DP are discussed in the section on Kinetics and Mechanisms.

Low-Velocity Detonation

Equilibrium calculation at 20 kbar and 1000 to 3000°K using the TIGER code has allowed us to calculate the possible the probable energy release under suspected LVD conditions for EN, 1,1-DNP, NM and 1,1-DNE. The calculated energy release coupled with the estimated shock pressure within the liquids showed that the previously reported correlation between the ratio of the heat of reaction to the heat of vaporization and the LVD gap sensitivity does not hold for the dinitro-alkanes.

Equilibrium calculations also indicate that 1,1-DNE on a per cm³ basis has more energy release than 1,1-DNP in the region expected for LVD. This may indicate why 1,1-DNE will undergo LVD while 1,1-DNP does not. However, EN which exhibits LVD has a lower heat release than does 1,1-DNP which does not undergo LVD. This may indicate that nitrate esters will probably exhibit LVD more readily than nitroalkanes of equal energy release.

Kinetics and Mechanisms of Thermal Decomposition

The VLPP reactor has been further modified by addition of a new reactor cell which can be used at three different collision numbers, 176, 1930 and 29,000, thus providing reaction rates over a span of four orders of magnitude. Calibration experiments with i-PrI gave results in excellent agreement with published work. Kinetic parameters for five nitro-and dinitropropanes, 2-NP, 1,2-DNP, 1,1-DNP, 2,2-DNP, and 1,1,1-FDNP were measured and, as before, we found that the first two, nongeminate dinitroalkanes, have parameters consistent with elimination of HONO with activation energies of 39 to 41 kcal/mol, respectively, while the latter three geminate dinitropropanes undergo C-N scission with activation energies of about 47 kcal/mol for all three compounds.

High pressure experiments with NM have been carried out in a newly developed apparatus which permits us to control temperatures to within 1°C at pressures up to 30 kbar. At 10 kbar, our results with NM parallel those of IRL closely over a fiftyfold change in pressure and we find an increase in apparent activation energy with increasing pressure.

Vibrationally excited 1,2-bis(difluoramino)propane (1,2-DP) was produced from the reaction of propylene with N₂F₄ at 135°C. At 2 torr, the lowest pressure studied, better than 98% of the "hot" 1,2-DP was stabilized. The remaining molecules lost 3 moles of HF to form the

iminonitrile, $\text{NCC}(\text{NF})\text{CH}_3$. RRK theory was used to calculate an activation energy of 43 kcal/mole for the loss of HF from 1,2-DP, assuming an A-factor of $10^{13.5} \text{ sec}^{-1}$. There is no significant difference between the above Arrhenius parameters and those reported previously for the loss of HF from methyldifluoramine.

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GLOSSARY OF COMPOUNDS

| <u>Code Name</u> | <u>Structure</u> | <u>Chemical Name</u> |
|------------------|---|---------------------------------------|
| 1,1-DNP | $\text{CH}_3\text{CH}_2\text{CH}(\text{NO}_2)_2$ | 1,1-dinitropropane |
| 2,2-DNP | $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_3$ | 2,2-dinitropropane |
| 1,2-DNP | $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$ | 1,2-dinitropropane |
| 1,3-DNP | $\text{NO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$ | 1,3-dinitropropane |
| 2-NP | $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_3$ | 2-nitropropane |
| 1,1-DNE | $\text{CH}_3\text{CH}(\text{NO}_2)_2$ | 1,1-dinitroethane |
| EN | $\text{CH}_3\text{CH}_2\text{ONO}_2$ | ethyl nitrate |
| 1,1,1-FDNE | $\text{FC}(\text{NO}_2)_2\text{CH}_3$ | 1,1,1-fluorodinitroethane |
| FEFO | $[(\text{NO}_2)_2\text{CFCH}_2\text{O}]_2\text{CH}_2$ | bis(1-fluoro-1,1-dinitroethyl) formal |
| 1,2-DP | $\text{CH}_3-\overset{\text{CH}}{\underset{\text{NF}_2}{\text{CH}}} \text{CH}_2-\text{NF}_2$ | 1,2-bis(difluoramino)propane |
| 2,2-DP | $\text{CH}_3\text{C}(\text{NF}_2)\text{CH}_3$ | 2,2-bis(difluoramino)propane |
| IBA | $\begin{array}{c} \text{CH} \\ \\ \text{CH}_3-\overset{\text{CH}}{\underset{\text{NF}_2}{\text{C}}} \text{CH}_2\text{NF}_2 \end{array}$ | |
| IBA | $\begin{array}{c} \text{CH} \\ \\ \text{CH}_3-\overset{\text{CH}}{\underset{\text{NF}_2}{\text{C}}} \text{CH}_2\text{NF}_2 \end{array}$ | 1,2-bis(difluoramino)-2-methylpropane |
| 1,2-DB | $\text{CH}_3\text{CH}_2\overset{\text{CH}}{\underset{\text{NF}_2}{\text{CH}}} \text{CH}_2\text{NF}_2$ | 1,2-bis(difluoramino)butane |
| NM | CH_3NO_2 | nitromethane |
| TNM | $\text{C}(\text{NO}_2)_4$ | tetranitromethane |
| NG | $\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2$ | nitroglycerin |

I INTRODUCTION

Under the sponsorship of the Office of Naval Research (ONR), Stanford Research Institute is studying the fundamental sensitivity properties of liquid high-energy materials in order to define the minimum number of physical and chemical parameters of the system needed to predict detonation sensitivity. In this work we have been primarily concerned with: (a) detonability of the liquid phase, i.e., whether it will support a detonation wave, and the failure diameter for detonation; (b) the necessary conditions for initiating detonation and whether ease of initiation is related to structure; and (c) the mode of decomposition of the chemical structure and the relationship of the initial decomposition steps with the phenomena of (a) and (b).

In previous work on this contract,* these relationships were studied with isomeric difluoraminopropanes and butanes, and we are now studying nitro compounds in the analogous isomeric propane series. Thus a direct comparison between the two high-energy groups that are of most interest at present can be made, and basic knowledge can be obtained on the initiation and propagation properties of model liquid nitroaliphatic plasticizers.

This program consists of three primary tasks:

A. Physics and Chemistry of Detonation

The ultimate objective of studies of the physics and chemistry of detonation (Section II) is to correlate transient detonation phenomena, such as shock initiation and failure behavior, with the mode of decomposition. This objective involves: (a) measurement of failure diameters;

* Stanford Research Institute Project 4051, Final Report, "Sensitivity Fundamentals," March 1962 to February 1970.

(b) study of events in the liquids as shocks of various magnitudes enter; (c) measurements of reaction times at pressures and temperatures comparable to those encountered in initiating shocks; and (d) measurement, evaluation, and correlation of physical and thermochemical properties.

B. Low-Velocity Detonation Wave Characteristics of the Liquid Phase

The objectives of this program (Section III) are to determine under which conditions LVD will initiate and to relate this initiation to the chemical and physical properties of the materials. By comparing two classes of materials (i.e., the difluoramino and dinitro compounds) with such widely different thermochemical and kinetic properties, those factors which influence LVD initiation can be ascertained.

C. The Mechanism and Kinetics of Thermal Decomposition

Section IV of this research effort comprises a study of the decomposition behavior of shock-sensitive liquids at very low and very high pressures and attempts to describe a relationship between detonation phenomena and chemical mechanism, including the elementary rate steps.

II PHYSICS AND CHEMISTRY OF DETONATION

(Robert Shaw)

A. Introduction

We have completed the calculations of shock temperature using the C_v and $C_v(T)$ models for some dinitroalkanes and alkyl nitrates. We have completed experiments on the elimination of HF from vibrationally hot 1,2-DP and begun to study the static-high-pressure-decomposition of nitroalkanes. This work is reported in detail in the section on Kinetics and Mechanisms. Some experiments on shock initiation are reported below.

At the same time as we are going forward with new work, we are also trying to reduce the backlog of results that have appeared in Progress Reports, but have not been written up for journal publication. To reduce unnecessary duplication, only the titles and authors of papers submitted to journals are given in this report.

B. Shock Temperatures

Recently¹ a $C_v(T)$ model was developed for calculating shock temperatures of polyatomic liquids in the region of 100 kbar. The $C_v(T)$ model was developed as an extension of the constant C_v (Walsh-Christian) model for metals. The extension was an attempt to allow for an expected increase in the intramolecular vibrational heat capacity as the temperature increases along the Hugoniot. The C_v and $C_v(T)$ models were used to calculate shock temperatures of nitromethane,^{1,2} liquid TNT,² and four bis(difluoramino)alkanes.² In the case of both nitromethane and the bis(difluoramino)alkanes, shock temperatures were calculated as a function of preshock temperature.²

In the present work, shock temperatures were calculated as a function of pressure using the C_v and $C_v(T)$ models for nitromethane (NM) as a check on the calculation, for some dinitroalkanes (whose transient detonation properties are presently under investigation), for ethyl nitrate (EN) and for nitroglycerine (NG). EN and NG have been widely used in studies on the detonation of liquids. The dinitroalkanes were 1,1-dinitroethane (1,1-DNE), 1,1-dinitropropane (1,1-DNP), 1,1,1-fluoro-dinitropropane (1,1,1-FDNP), and 1,2-dinitropropane (1,2-DNP). The variation of C_v (ideal gas) with temperature for all compounds except NM was estimated by atom additivity.²

The input data are shown in Table I. The results for 1,1-DNE using the C_v model are shown as an example in Table II. Shock temperatures were fitted to a fifth-order polynomial in pressure, as shown graphically in Fig. 1 for 1,1-DNE. Shock temperatures for all the liquids, calculated using both the C_v and $C_v(T)$ models, are listed at 50-kbar intervals to 200 kbar in Table III.

I know of no measured or calculated shock temperatures with which to compare the present results. Perhaps the most notable feature of the results is that, at any given pressure, nitromethane has the highest shock temperature and nitroglycerine has the lowest shock temperature.

C. Shock Initiation

Work has begun on the measurement of smooth shock reaction times of the dinitroalkanes. Results for 1,1-DNE and 1,1-DNP at an initial preshock temperature of 25°C are compared with previous results for NM in Figure 2. When the reaction times are plotted as a function of peak pressure in the attenuator, for constant reaction time, the shock pressure increases in the order 1,1-DNE, NM, and 1,1-DNP. This is the order found by Woolfolk in gap test measurements (gaps at $20 \pm 5^\circ$ were

Table I Input Data for Shock Temperature Calculations

| Quantity | Units | NM ² | 1,1-DNE ^d | 1,1-DNP ^d | 1,1,1-FDNP ^d | 1,2-DNP ^d | EN ^e | NG ^f |
|--|--|-----------------|----------------------|----------------------|-------------------------|----------------------|-----------------|-----------------|
| ($\partial p/\partial T$) ^a | 10^7 dyn cm^{-2} deg ⁻¹ | 1.63 | 1.58 | 1.65 | 1.12 | 1.45 | 1.24 | 2.22 |
| Sound speed | 10^5 cm sec ⁻¹ | 1.3 | 1.27 | 1.39 | 1.04 | 1.34 | 1.08 | 1.44 |
| Specific volume at $p = 0$ | cc g ⁻¹ | 0.884 | 0.738 | 0.797 | 0.753 | 0.758 | 0.908 | 0.629 |
| Molecular wt | g mol ⁻¹ | 61 | 120.1 | 134.1 | 152.1 | 134.1 | 91.1 | 227.1 |
| C_v^b (constant) | cal mol ⁻¹ deg ⁻¹ | 17.8 | 37.9 | 43.4 | 43.8 | 45.0 | 36.2 | 60.5 |
| C_v fit ^c : | $10^{-6}B$ | 1.23375 | 1.23375 | 3.044 | 3.044 | 45.0 | 2.356 | 11.37 |
| | $10^{-4}C$ | -0.995686 | | -2.506 | | | -1.882 | -8.183 |
| | $10^{-1}D$ | 1.73573 | | 5.092 | | | 3.432 | 16.83 |
| | 10^3E | 8.09421 | | -3.368 | | | 9.771 | -70.87 |
| | 10^6F | -2.24624 | | 0.8369 | | | -4.354 | 15.16 |

^aCalculated from $(\partial p/\partial T)_v = \alpha C_v C_o^2/V_o C_p$ where α is the coefficient of expansion C_o , V_o is the specific volume at $p = 0$, C_v is the heat capacity at constant volume, and C_p is the heat capacity at constant pressure.

^b C_v was calculated from $C_v = C_p / [1 + (IMT\alpha^2 C_o^2) / (2.39 \times 10^{-8}) C_p]$ where M is the molecular weight and 2.39×10^{-8} corrects the units $C_v(T)$ is given by $C_v(\text{constant}) + (B/T^2) + (C/T) + D + E \times T + F \times T^2$.

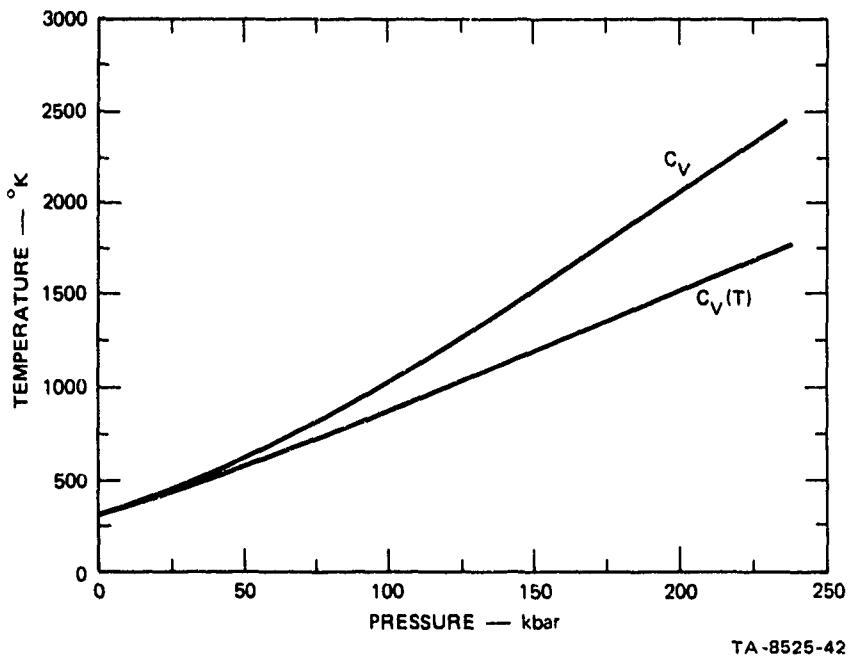
^cThe physical properties V_o , α , C_p , C_v , and C_o have been measured by R. Shaw (unpublished work).

^d C_p was estimated from $C_p = C_p' / [1 + (IMT\alpha^2 C_o^2) / (2.39 \times 10^{-8}) C_p]$. R. Shaw, J. Chem. Eng. Data 14, 461 (1969) and D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969). V_o was obtained and α was calculated from the average of results by R. Shaw (unpublished work) and data in *Handbook of Chemistry* (ed Lange, McGraw-Hill, New York, 1961), 10th ed. The sound speed was measured by R. Shaw (unpublished work).

^e V_o was obtained and α was calculated from J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York, 1960 and 1965), Vols. I and II. The sound speed was measured by R. Gates and R. Shaw (unpublished work). C_p was reported by T. Urbanski, *Chemistry and Technology of Explosives* (Pergamon, New York, 1965), p. 45.

Table II Calculation of the Shock Temperature of 1,1-Dinitroethane Using the Constant C_v (Walsh-Christian) model.

| Pressure, kbar | Volume, cc/g | Particle Velocity, mm/ μ sec | Temperature, °K | Shock Velocity, mm/ μ sec |
|-------------------|-----------------|--|--------------------|-------------------------------------|
| 0.0 | 0.738 | 0.00 | 298 | 1.524 |
| 5.1 | 0.659 | 0.20 | 330 | 1.864 |
| 11.9 | 0.604 | 0.40 | 364 | 2.204 |
| 20.7 | 0.564 | 0.60 | 410 | 2.544 |
| 31.3 | 0.533 | 0.80 | 472 | 2.884 |
| 43.7 | 0.509 | 1.00 | 555 | 3.224 |
| 58.0 | 0.490 | 1.20 | 661 | 3.564 |
| 74.1 | 0.473 | 1.40 | 792 | 3.904 |
| 92.0 | 0.460 | 1.60 | 948 | 4.244 |
| 111.8 | 0.448 | 1.80 | 1131 | 4.584 |
| 133.4 | 0.438 | 2.00 | 1341 | 4.924 |
| 156.9 | 0.430 | 2.20 | 1579 | 5.264 |
| 182.2 | 0.422 | 2.40 | 1845 | 5.604 |
| 209.4 | 0.415 | 2.60 | 2140 | 5.944 |
| 238.4 | 0.409 | 2.80 | 2463 | 6.284 |
| 269.3 | 0.404 | 3.00 | 2816 | 6.624 |

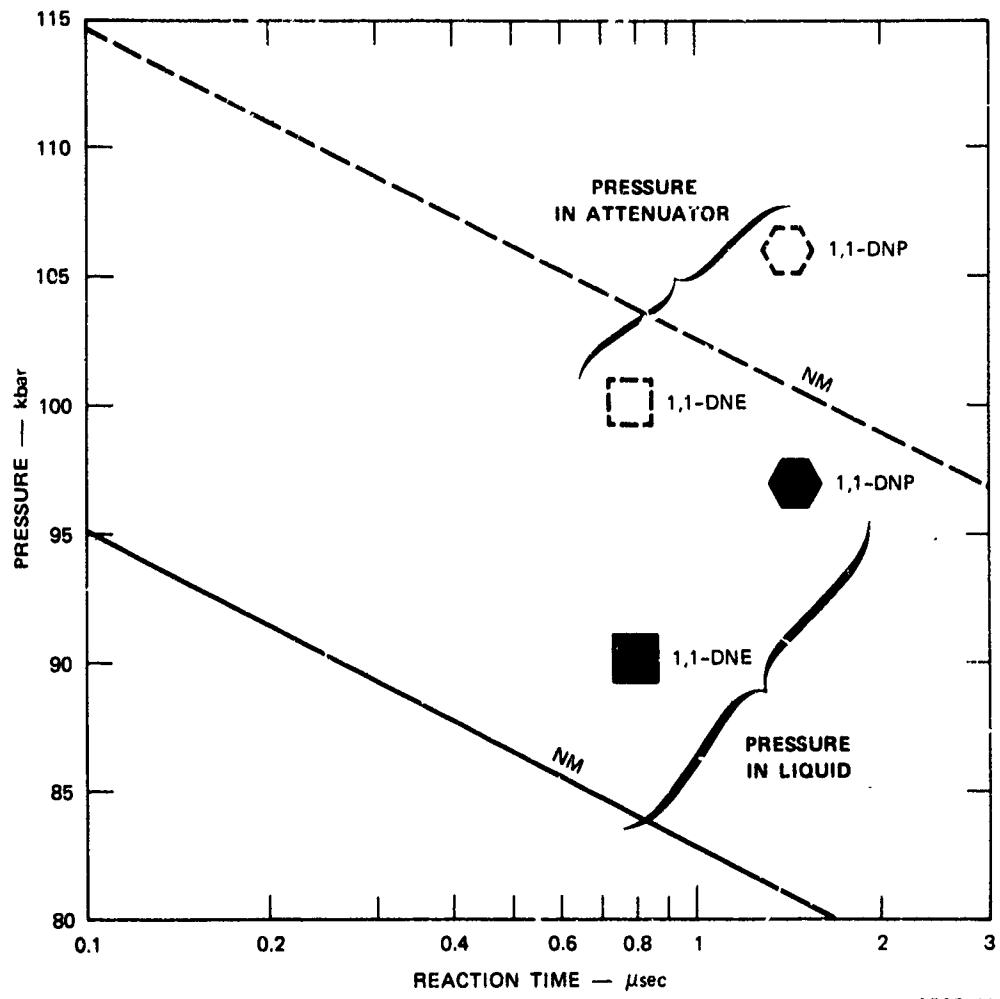


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FIGURE 1 SHOCK TEMPERATURE OF 1,1-DNE CALCULATED USING THE C_V AND $C_{V(T)}$ MODELS

Table III Calculated Shock Temperature for Some Nitroalkanes and Alkyl Nitrates as a Function of Shock Pressure Using the C_V and $C_V(T)$ models.

| Liquid | Model | Pressure, kbar | | | |
|-----------------------|----------|----------------|------|------|------|
| | | 50 | 100 | 150 | 200 |
| Shock Temperature, °K | | | | | |
| NM | C_V | 738 | 1318 | 1988 | 2704 |
| NM | $C_V(T)$ | 639 | 978 | 1324 | 1667 |
| 1,1-DNE | C_V | 602 | 1019 | 1508 | 2037 |
| 1,1-DNE | $C_V(T)$ | 579 | 881 | 1196 | 1517 |
| 1,1-DNP | C_V | 596 | 1008 | 1496 | 2026 |
| 1,1-DNP | $C_V(T)$ | 551 | 835 | 1135 | 1441 |
| 1,1,1-FDNP | C_V | 674 | 1198 | 1795 | 2433 |
| 1,1,1-FDNP | $C_V(T)$ | 609 | 958 | 1316 | 1679 |
| 1,2-DNP | C_V | 569 | 956 | 1413 | 1910 |
| 1,2-DNP | $C_V(T)$ | 532 | 805 | 1094 | 1389 |
| EN | C_V | 652 | 1125 | 1660 | 2228 |
| EN | $C_V(T)$ | 592 | 905 | 1223 | 1544 |
| NG | C_V | 585 | 962 | 1410 | 1906 |
| NG | $C_V(T)$ | 538 | 785 | 1048 | 1327 |



TA-8525-41

FIGURE 2 SMOOTH SHOCK REACTION TIME MEASUREMENTS FOR 1,1-DNP AND 1,1-DNE COMPARED WITH EARLIER DATA FOR NM

1.42 ± 0.16 cm for 1,1-DNE; 1.27 ± 0.03 cm for NM; and 1.05 ± 0.03 cm for 1,1-DNP; the smaller the gap, the higher the peak pressure in the liquid). On the other hand, when the reaction times are plotted as a function of peak pressure in the liquid, using impedance matching, for constant reaction time, the shock pressure increases in the order NM, 1,1-DNE, and 1,1-DNP. The change in ordering occurs because NM has a significantly lower density at $\rho = 0$ than the two dinitroalkanes, that results in a lower shock pressure in the liquid for a given attenuator pressure.

In terms of homogeneous thermal explosion theory, at first sight the higher reactivity of NM compared with 1,1-DNE and 1,1-DNP is surprising because the C-N bond strength in NM is about 12 kcal mole $^{-1}$ stronger than in the dinitro compounds. However, the shock temperature calculations show that for a given shock pressure the shock temperature on NM is significantly higher than for the two dinitro compounds. For example, at 100 kbar, using the C_v (Walsh-Christian) model shock temperatures in $^{\circ}\text{K}$ were NM, 1318 ; 1,1-DNE, 1019 ; and 1,1-DNP, 1008 . Thus the faster reaction of NM compared with the dinitroalkanes may be due to the higher shock temperature than to purely chemical effects. The answer to this question ought to be provided by the static high-pressure experiments.

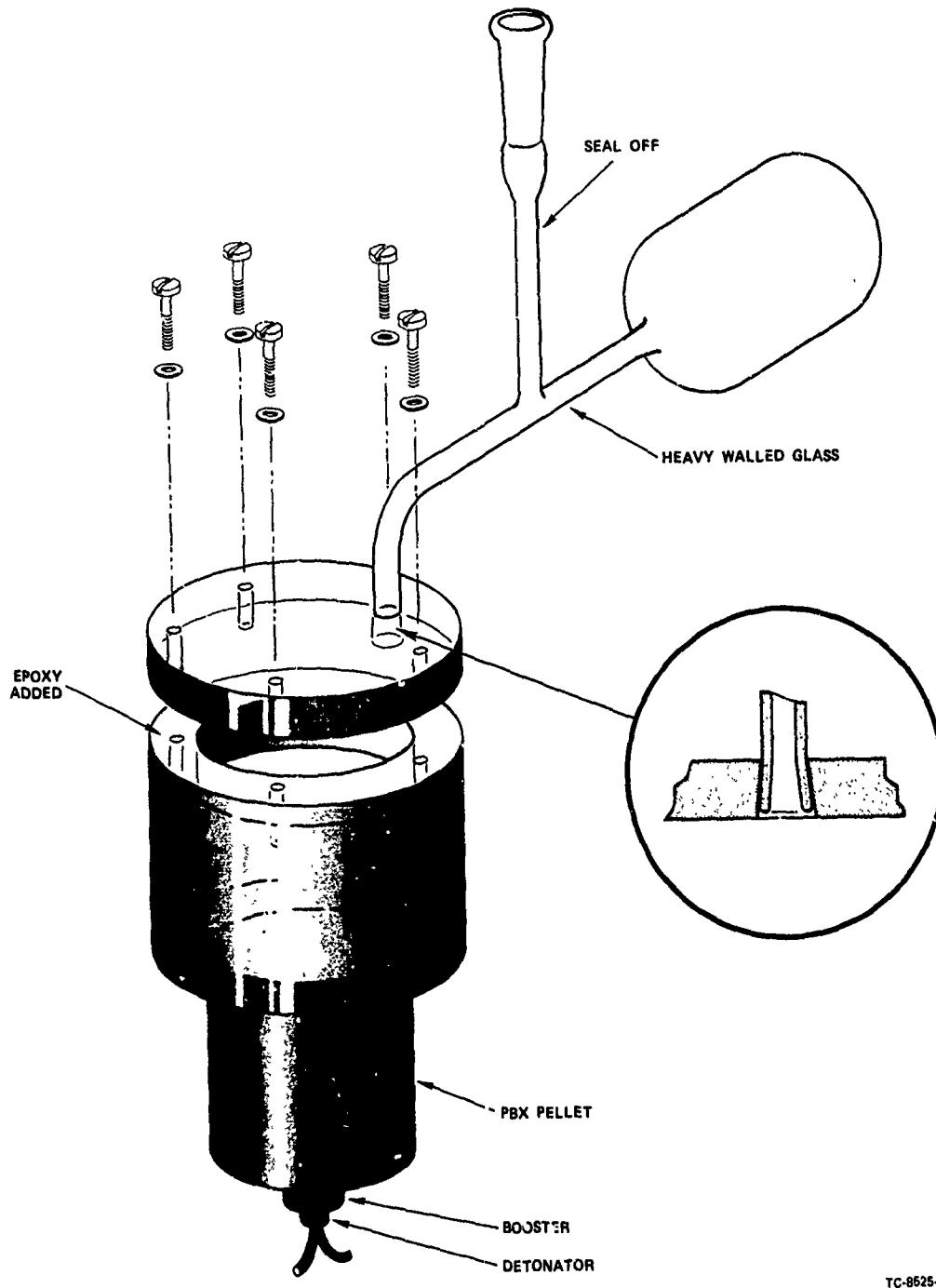
Over the past few years we have been flirting with methyl nitrite, CH_3ONO . This compound is attractive because it is an isomer of nitromethane and has a very similar heat of formation, entropy, and free energy of formation, but its kinetics of decomposition are very different from those of nitromethane due to the weak (~ 40 kcal mole $^{-1}$) $\text{CH}_3\text{O-NO}$ bond. The only problem with methyl nitrite is its volatility. In previous work, this was overcome by working at very low temperatures. However, this approach led to other problems such as the possibility of freezing the methyl nitrite, and it made difficult a comparison with ambient

temperature results. Therefore the alternative approach of working at higher pressures was used. The vapor pressure of methyl nitrite at 25°C is about 10 atmospheres. This is still negligible compared to shock pressure and is reasonable for making a reaction cell assembly. The experimental arrangement is shown in Figure 3. Methyl nitrite was synthesized and condensed in the glass bulb, the entry tube was sealed, and the detonator and booster assembly was attached while the methyl nitrite was still condensed in the bulb by a bath at -80°C. Just before the shot was fired, the bath was removed, the methyl nitrite was allowed to warm up to 25°C, and the shot assembly was tilted to fill the reaction cell. There was very little problem with bubbles because the methyl nitrite had been condensed under vacuum and no air was present.

The attenuator thickness corresponded to a shock pressure in the liquid methyl nitrite of 45 kbar. This low pressure was chosen because in all previous experiments with methyl nitrite, the methyl nitrite had initiated so that no lower limit of shock pressure had been established. The present experiment failed to initiate, giving the desired lower limit. Further experiments are underway with thinner attenuators, corresponding to higher shock pressures, to obtain initiation and therefore a measurable reaction time.

D. Future Work

For the remainder of the current year, the main emphasis will be on writing up past results and on the static higher pressure experiments. In addition, the shock initiation studies on 1,1-DNE, 1,1-DNP, and methyl nitrite will be completed. If time permits, a start will be made on dark wave experiments with the dinitroalkanes.



TC-8625-40

FIGURE 3 CELL FOR REACTION TIME MEASUREMENTS FOR METHYL NITRITE AT 10 ATMOSPHERES PRESHOCK PRESSURE

E. Publications

The following papers resulting from this work have been submitted for journal publication:

1. "Densities and Sound Speeds of Some Liquid Dinitroalkanes and Alkyl Nitrates," R. W. Gates and R. Shaw, J. Chem. Eng. Data.
2. "Heat Capacities of Some Nitroalkanes," W. E. Robbins and R. Shaw, J. Phys. Chem.
3. "Calculated Shock Temperature of Some Liquid Nitroalkanes and Alkyl Nitrates," R. Shaw, J. Chem. Phys.
4. "The Kinetics of the Unimolecular Dehydrofluorination of 1,2-Bis(difluoramino)propane," D. S. Ross and R. Shaw, Int. J. Chem. Kinetics.

F. Acknowledgments

G. S. Cartwright was the site leader on the shock initiation experiments. The pressure reaction cell for the methyl nitrite shot was made by J. H. Hannigan with help from J. W. Van Gastel.

III LOW-VELOCITY DETONATION

(R. Woolfolk)

A. Introduction

The relationship between chemical structure and low-velocity detonation (LVD) sensitivity is the concern of this portion of the program. We are studying the presence of LVD in model compounds which are related structurally to candidate monopropellants and explosive plasticizers. In particular, we are attempting to relate the LVD gap sensitivity of these model compounds with their thermodynamic and kinetic properties.

We define LVD as a reaction wave propagating at a velocity supersonic with respect to the unreacted liquid but slower than a conventional high-velocity detonation (HVD). When compared with HVD, the initiation and propagation of LVD is a substantially more complex phenomenon.

In the dinitroalkanes isomeric series the propane isomers do not undergo LVD, but 1,1-DNE does. We have shown³ that the differences in LVD sensitivity can not be attributed to initial decomposition kinetics as these are nearly identical for both 1,1-DNE and the corresponding dinitropropane (1,1-DNP). In the search for an alternative explanation we have been examining the energy release expected in LVD to determine if a minimum energy was required to propagate LVD. Now that we have two liquid explosives with very similar physical properties -- one of which does not undergo LVD, we feel we are much closer to sorting out some of the chemical factors that influence LVD.

B. Experimental and Theoretical Studies

We have refined our previous determination of the LVD gap sensitivity of EN, using our standard LVD gap test which consists of a steel tube

10.4 cm long, 1.27 cm i.d. and 0.25 cm wall, boosted by a 100-g tetryl donor and attenuated by Plexiglas. The results are shown in Table IV.

Table IV

LVD GAP SENSITIVITY OF EN

| Gap Plexiglas (cm) | Camera + go; - no go | Temperature (°C) |
|--------------------------|-------------------------|---------------------|
| 4.6 | - | 20 |
| 3.8 | - | 21 |
| 3.1 | + | 20 |

The presence of LVD was detected by the use of a framing camera.³ Therefore, the LVD gap sensitivity for EN lies between 3.1 and 3.8 cm; previously reported values were 3.8-5.1 cm.

To determine the energy available to propagate LVD, we have run a series of TIGER calculations for conditions under which we believe LVD takes place. The TIGER code is an advanced computer code to calculate hydrodynamic and thermodynamic properties under shock and detonation conditions. We have used only the thermodynamic portions of the program for our calculations. Figures 4 through 7 show the equilibrium products expected for four explosive liquids as a function of temperature at 20 kbar. It is interesting to note how important the water-gas reaction (equation 1) is in this region. For example, as shown in Figure 4 when



1,1-DNP reacts in the temperature range 1000-3000°K, the mole percent of solid carbon goes from 30 to 0 when the temperature is raised from

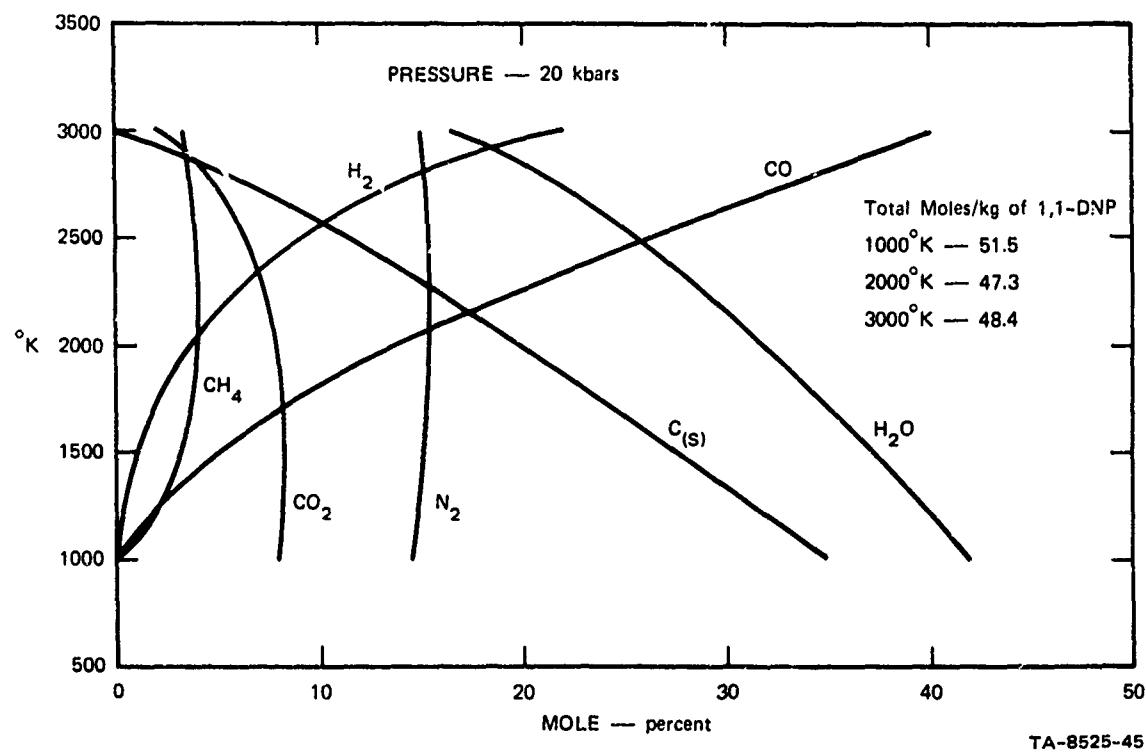


FIGURE 4 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1-DNP (Tiger)

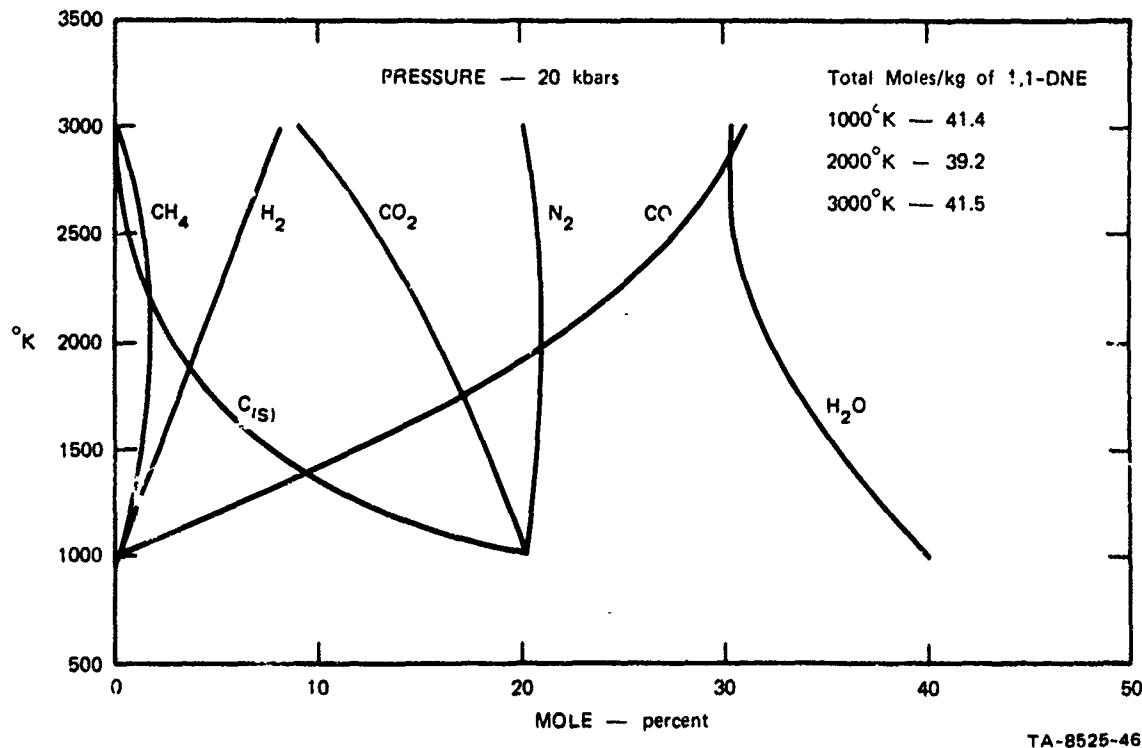


FIGURE 5 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR 1,1-DNE (Tiger)

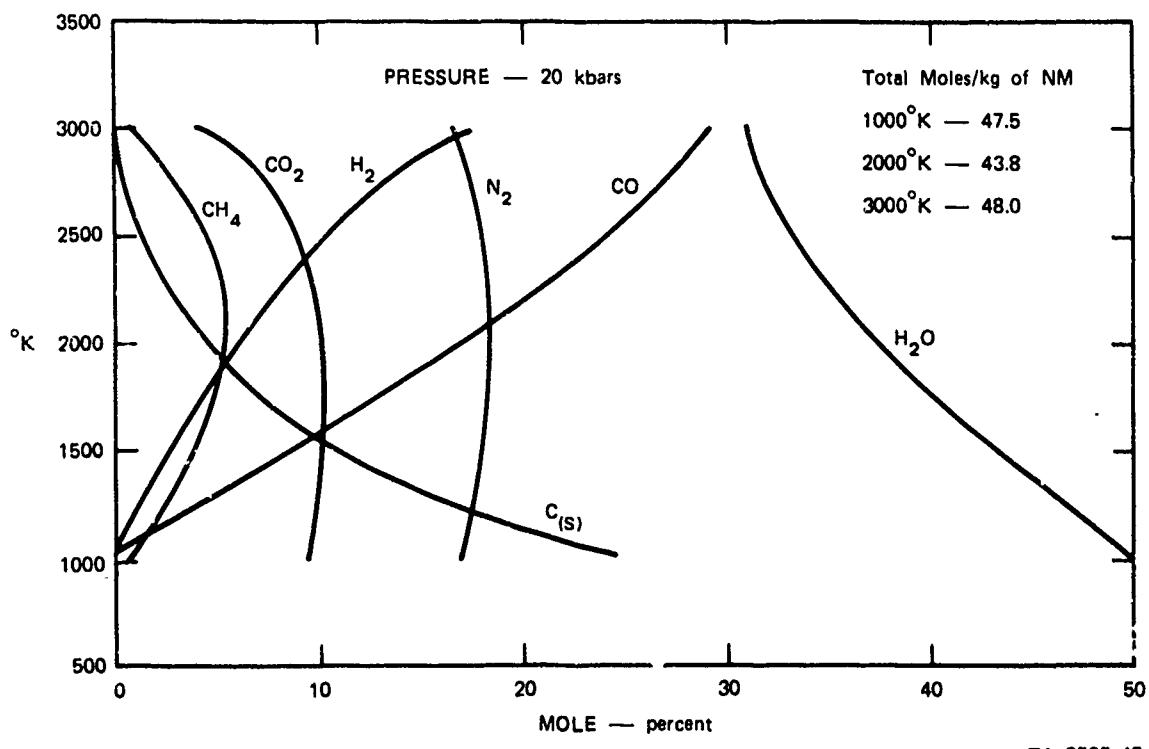


FIGURE 6 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR NM (Tiger)

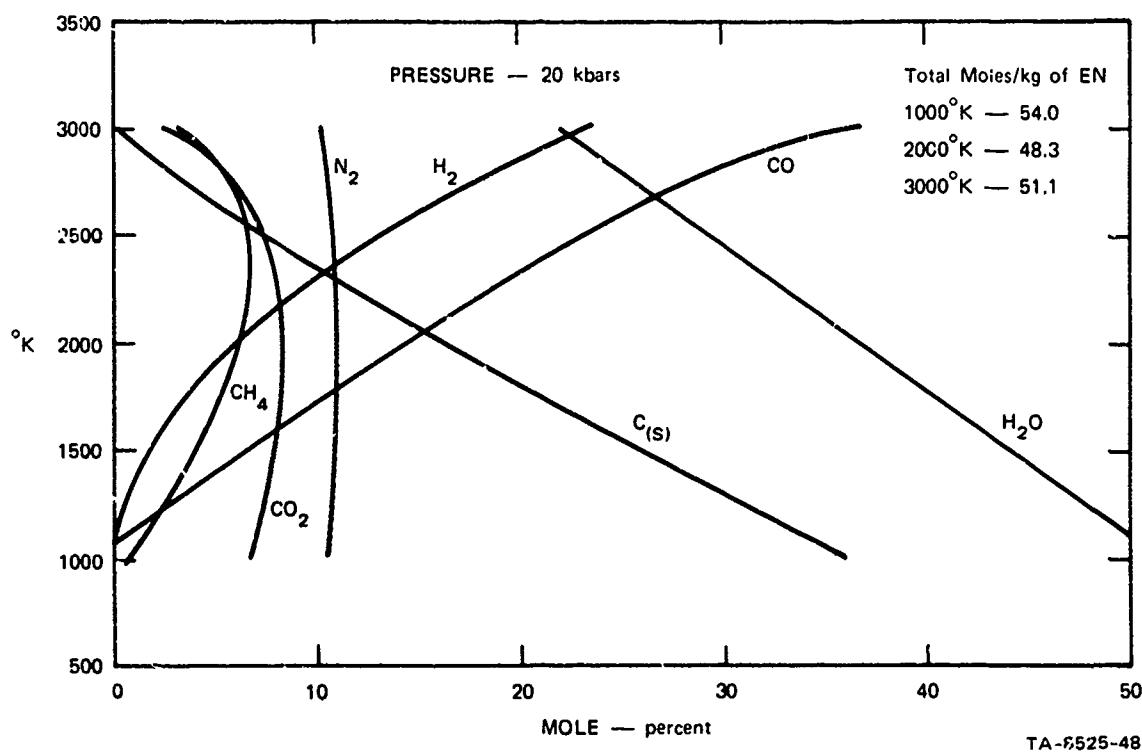


FIGURE 7 MOLE PERCENT AS A FUNCTION OF TEMPERATURE FOR EN (Tiger)

1000 to 3000°K. Since this reaction is endothermic it has the effect of lowering the total available energy. Therefore in low oxygen balance compounds (high product carbon) relatively more energy is lost when the temperature rises than in compound more nearly balance to CO to CO₂.

C. Discussion

The two-stage process that we now believe constitutes LVD explains why both the properties of the explosive liquid and its confinement play important roles in determining LVD sensitivity. LVD can be viewed as a reactive wave propagating in a cavitated medium. Therefore, before LVD can occur, cavitation of the liquid is necessary. This cavitated liquid must then be initiated and, in a steady-state process, sufficient energy must be generated to produce further cavitation upstream of the reaction site. Thus, confinement parameters that increase cavitation or allow energy transfer for cavitation ahead of the reaction zone increase the apparent LVD sensitivity of the liquid. This we have shown to be the case.⁴ The above model also leads us to postulate that increasing the heat of reaction ΔH_r (energy available) would increase the sensitivity, and decreasing the heat of vaporization ΔH_v would also increase the sensitivity by requiring less energy to cavitate the liquid. Therefore we attempted to correlate the ratio of $\Delta H_r / \Delta H_v$ with the LVD gap sensitivity.

We had some initial indication that this correlation was useful, but the difficulty arose in determining ΔH_r as we were not sure under what conditions LVD reactions were taking place. For instance, this correlation predicted that LVD should occur in the DNPs but it did not.

In addition, using the data we had obtained on nitro-containing explosive liquids as well as on a nitrate ester (ethyl nitrate), we were able to show³ that increasing the oxygen balance increased the likelihood

of LVD. As oxygen balance is just another measure of energy release, we decided to perform the TIGER calculation to define ΔH_r more concisely. These data would also enable us to check the correlation between gap sensitivity and $\Delta H_r / \Delta H_v$.

The predicted temperatures (TIGER) for the conventional high velocity detonation are 2650°K for 1,1-DNP and 2900°K for 1,1-DNE. It seems reasonable, therefore, that the temperatures expected for the LVD reaction in these materials would lie below those values. Table V lists the energy release for 1,1-DNE, 1,1-DNP, NM and EN at 20 kbar and at temperatures of 1000 and 2000°K.

Table V

ENERGY RELEASE FOR 1,1-DNE, 1,1-DNP, NM, AND EN AT 20 KBAR

| Compound | Density of Liquid (g/cc) | ΔH_r (kcal/mole) | Temperature (°K) | ΔH_r | | $\Delta H_r / \Delta H_v$ |
|----------|--------------------------------|-----------------------------|---------------------|--------------|------------|---------------------------|
| | | | | (kcal/mole) | (kcal/cm³) | |
| NM | 1.14 | 9.09 ^a | 1000 | -88 | -1.64 | 9.7 |
| NM | 1.14 | | 2000 | -74 | -1.38 | 8.05 |
| 1,1-DNP | 1.26 | | 1000 | -182 | -1.71 | 12.2 |
| 1,1-DNP | 1.26 | 14.9 ^a | 2000 | -162 | -1.52 | 10.9 |
| 1,1-DNE | 1.37 | | 1000 | -175 | -2.00 | 12.1 |
| 1,1-DNE | 1.37 | 13.9 ^b | 2000 | -155 | -1.77 | 11.1 |
| EN | 1.11 | | 1000 | -121 | -1.48 | 13.8 |
| EN | 1.11 | 8.7 ^a | 2000 | -111 | -1.35 | 12.8 |

a. Obtained from vapor pressure curves.

b. Estimated from 1,1-DNP by group additivity (Ref. 4).

A comparison of the ΔH_r on a heat release per cm^3 basis shows that 1,1-DNE has more energy available in this temperature range than either NM or 1,1-DNP observation. This may indicate why 1,1-DNE will sustain LVD, but NM and 1,1-DNP will not. However such a correlation does not explain why EN undergoes LVD and leads to the speculation that the discrepancy may be due to other factors peculiar to nitrate esters.

To make a more meaningful correlation when using gap sensitivities, one should compare the shock pressure in the liquid produced by the initiating shock. To estimate this parameter, impedance matching was used.^{5,6} Equation (2),

$$\frac{P_1}{P_e} = \frac{\rho_e D_e + \rho_1 D_1}{2\rho_e D_e} \quad (2)$$

where subscript 1 stands for Plexiglas donor, e stands for the explosive, P is the pressure, D is the shock velocity, and ρ is the density, was used to calculate the pressure in the liquid explosive. Since we did not measure the shock velocity in liquid explosive nor the Plexiglas donor, we can estimate the pressure by using a zero-order correction in which the shock velocity is replaced by the sound velocity (C_o). For the weak shocks and low pressures found in the initiation of LVD, this is a reasonable method. Table VI gives the results of these calculations for the four materials that are given in Table V.

perhaps that is like comparing apples and oranges. On the other hand, it may indicate that nitrate esters are inherently more sensitive to LVD than nitro compounds. Therefore it might be concluded that, to synthesize compounds less prone to LVD, it is better to use nitro groups than nitrate esters. To develop this postulate, we are now attempting to determine ΔH_r for the difluoramino materials previously studied and make comparisons between the nitroalkanes, nitrate esters and the difluoraminoalkanes.

D. Future Work

During the next period, we will be conducting experiments on the effects of temperature on LVD gap sensitivity. Originally we had planned to use the DNPs for this study, but they did not exhibit LVD even at 60°C. Therefore we will use 1,1-DNE for these studies, and perhaps even study ethyl nitrate to provide additional data. 1,1,1-FDNE is now being prepared for studies, as well as 1,1,1-fluorodinitromethane. These materials will enable us to further our studies on the effects on the LVD sensitivity of replacement of an H-atom by a fluorine.

We will continue an analysis of the TIGER calculation for the difluoramino compounds to investigate further the thermodynamic properties that influence LVD initiation.

We are also planning to study what effect the addition of amines to nitro compounds has on their LVD sensitivity. It is well known that the addition of a small quantity of amines to nitromethane increases its HVD sensitivity.⁷ We will add small amounts of amines to both 1,1-DNE and 1,1-DNP to see how they affect the LVD sensitivity of the former and if they cause LVD to appear in the latter.

Table VI

ESTIMATION OF INPUT SHOCK PRESSURES

| Material | ρ_o (cg/cc) | C_o (mm/ μ sec) | LVD Gap ^a (cm) Plexiglas | P_1^c (kbar) | P_e (kbar) |
|----------|---------------------|--------------------------|--|-------------------|-----------------|
| EN | 1.11 | 1.08 | 3.1-3.8 | 38 | 22 |
| 1,1-DNE | 1.37 | 1.3 | 6.4-8.3 | ~12 | ~9 |
| NM | 1.13 | 1.3 | 1.30 ^d | 67 | 46 ^d |
| 1,1-DNP | 1.26 | 1.38 | 1.02 ^d | 72 | 55 ^d |

a. Gap reported for 100-g tetryl donor and steel tube 10.4 cm long, 1.27 cm i.d., and 0.25 cm wall.

b. Input parameters for Plexiglas: $\rho_o = 1.18$ $C_o = 2.4$ mm/ μ sec

c. See Ref. 6

d. Represents HVD initiation as no LVD present. First-order calculation using C_o instead of D_e not too valid at these pressures.

By examining the data in Tables V and VI especially for 1,1-DNE and 1,1-DNP, one can see that there is little correlation between $\Delta H_r / \Delta H_v$ and the gap sensitivity. 1,1-DNE and 1,1-DNP have a value for this parameter at 2000 and 1000°K that agrees within experimental error, yet one can be initiated to LVD by a pressure of about 10 kbar whereas the other does not initiate LVD even at 5 to 6 times this pressure.

The idea that there may be a critical energy for LVD propagation is indicated by the ΔH_r values for 1,1-DNE and 1,1-DNP. But this value must be relative and useful only where comparing very similar compounds as EN has a value for ΔH_r below both NM and 1,1-DNP yet undergoes LVD. Because EN is a nitrate ester while both NM and 1,1-DNP are nitro compounds,

IV KINETICS AND MECHANISMS OF DECOMPOSITION

(D. S. Ross, L. Piszkiewicz, and P. De Carli)

A. Introduction

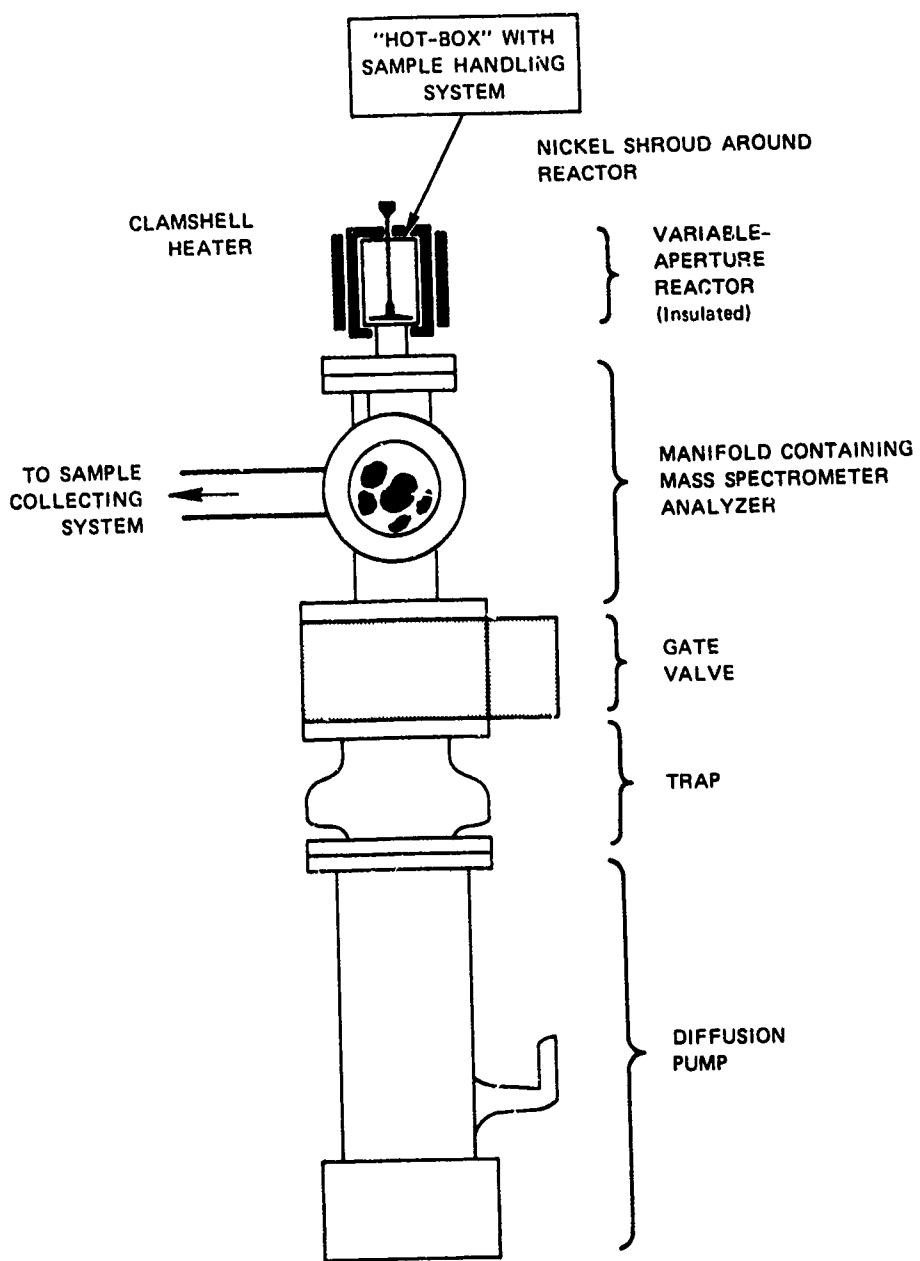
In our last report⁵ we discussed some results we had obtained in our very-low-pressure pyrolysis (VLPP) studies of several nitropropane. The results, although useful in defining trends in stability, were not reliable due to design deficiencies in the VLPP reactor assembly. In this report we present more reliable data for the unimolecular decomposition of the same compounds obtained in our new, calibrated reactor. With these results now in hand, we have concluded the VLPP studies.

We have also assembled a well-controlled high-pressure apparatus for static high-pressure studies initially using NM. Some initial results are reported here.

B. VLPP Studies

We have concluded our VLPP study of several nitroalkanes in our new reactor. This reactor system features an efficient and high-speed pumping system with the mass spectrometer head positioned immediately below the reactor orifice (Fig. 8). The new pumping system has eliminated the problem of back diffusion found in the old system.

The reactor can be operated at three different collision numbers. This objective is attained through an assembly in which a cutaway quartz disk with two holes and a polished bottom surface rests on the polished upper surface of the base of the reactor. The disk can be rotated by means of a rod passing from an external control knob down through the center of the reactor. A hole through the reactor base 10.3 mm in diameter



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FIGURE 8 NEW VLPP ASSEMBLY

is located off-center, such that the upper plate can be positioned to expose the base hole through the cutaway portion of the plate. This alignment provides a collision number of 176.

Alternatively, the plate can be rotated such that one of its holes is positioned over the base hole, reducing the area of the exit aperture of the reactor, and increasing the collision number of the system. A 3.1-mm plate hole provides a collision number of 1930, and an 0.81-mm hole, 29,000 collisions (see Fig. 9). This multicollision number arrangement allows us to measure reaction rates over better than four orders of magnitude.

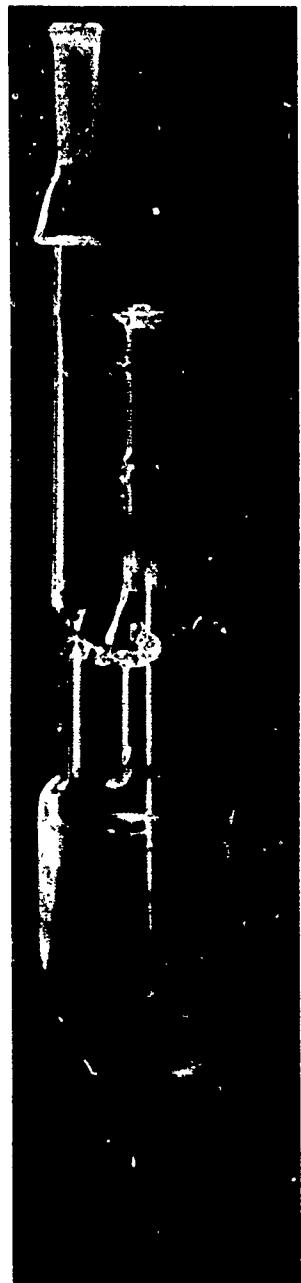
The first runs with the new apparatus were with i-PrI for which kinetic data, including VLPP data, are known.⁹ Our calibrating results are in excellent agreement with these.

Our results for the nitroalkanes are presented in Table VII.

Table VII
VLPP KINETIC DATA FOR SOME NITROALKANES

| Compound | Log A (sec ⁻¹) | E _a (kcal/mole) | |
|--------------|-------------------------------|----------------------------|-----------------------------|
| | | Current Values | Earlier Values ^a |
| 2-NP | 11.3 | 39 ± 1 | -- |
| 1, 2-DNP | 11.5 | 41 ± 1 | 42 |
| 1, 1-DNP | 17.5 | 47 ± 1 | 49 |
| 2, 2-DNP | 17.5 | 46 ± 1 | 49 |
| 1, 1, 1-FDNP | 17.5 | 47 ± 1 | 49 |

^a Reference ⁵



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FIGURE 9 MULTICOLLISION NUMBER ARRANGEMENT FOR VLPP REACTOR

The above data show that the differences between the old and new results are small. However, in view of the calibration experiments with i-PrI, we believe the new data are more reliable and useful in the treatment of the detonation of nitroalkanes.

The gem-dinitroalkanes, 1,1-DNP, 2,2-DNP, and 1,1,-FDNP, all undergo C-N scission and at about the same rate. Thus the C-N bond strength in each of the three molecules is 46 to 47 kcal/mole and apparently, the effects on the C-N bond strength of H-, CH₃-, and F-substitution on the (NO₂)₂ bearing carbon are nominally the same. The nongeminate material 1,2-DNP, on the other hand, has a C-N bond strength of ~60 kcal/mole, and undergoes cyclic elimination of HONO. Comparing 2-NP with 1,2-DNP shows that the second NO₂ in the dinitro compound seems to have little effect on the elimination rate.

This concludes our VLPP study, and these results will shortly be prepared for publication.

C. Static High Pressure Thermal Decomposition Studies

Procedure

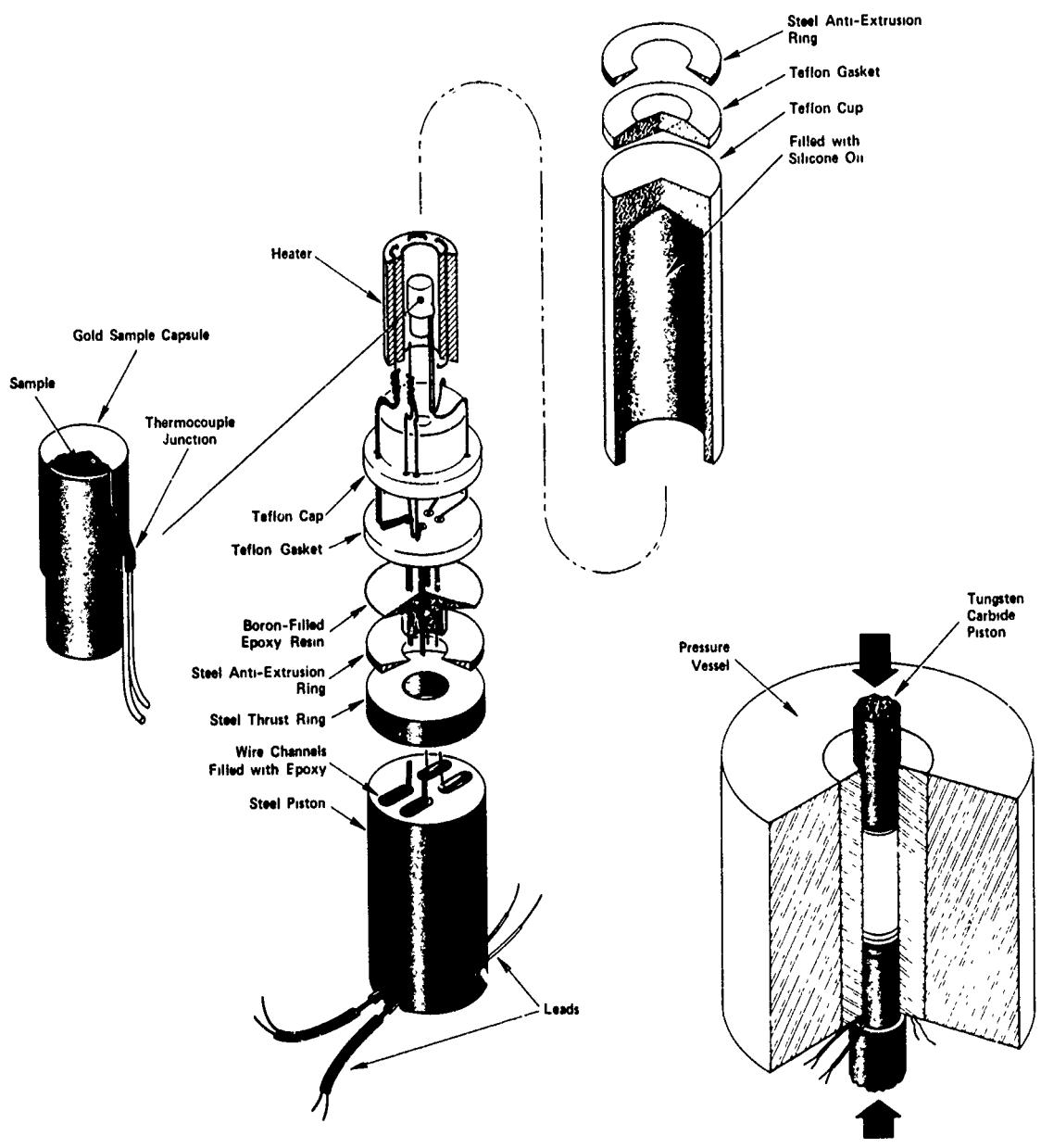
Results of thermal decomposition studies of various explosives under conditions of high pressure static loading have been previously reported by Lee et al.¹⁰ They performed decomposition studies at confining pressures of 10 and 50 kbar and found the decomposition kinetics of four compounds (PETN, HMX, nitromethane, and 2,2-DNP) to be markedly altered by high confining pressures. However, they pointed out that their results were qualitative in nature, for they were unable to measure or control sample temperatures with the accuracy required for precise kinetic studies. From the results of calibration experiments, they inferred that the accuracy of their temperature measurements was about ±15° C. They did not comment on the accuracy of

their pressure estimates, but we note that their conclusions would not be affected by pressure errors of $\pm 20\%$, a figure which we estimate is appropriate to their experimental arrangement.

In the present work, we have concentrated our efforts on developing an experimental technique which permits much greater accuracy and control of sample temperature in the high pressure environment. Accordingly, we have adapted the "Teflon cell" technique¹¹ to the requirements of the present program. The Teflon cell geometry is shown in Figure 10.

The sample under investigation is loaded into a gold sample container of the double cup type, obtained from the same source as those used by Lee et al. As supplied, the cups do not fit together well enough to form a liquid-tight seal. We have found it necessary to swage the closed end of the larger cup to a slightly smaller diameter. To avoid the possibility of air bubbles in the sample liquid, the container is assembled and sealed while immersed in the liquid. A small lip, similar to a pouring lip, is formed in the outer gold cup. A Chromel-Alumel thermocouple is inserted into the space between the lip and the inner cup, and the lip is then crimped down to hold the thermocouple in place.

The sample container is surrounded by a heater assembly; the sample thermocouple-heater assembly is placed in a silicone oil-filled Teflon cell, and the Teflon cell is placed in a conventional piston-cylinder apparatus. When force is applied to the piston, the sample is subjected to a hydrostatic pressure transmitted by the silicone oil, which also serves as a heat transfer medium. The Teflon cell is a very effective leakproof container at high pressures, and the system has low friction. The pressure in the fluid can be calculated from the force-piston diameter relationship with an accuracy of about 5%. Hanneman and Strong¹² have found the effect of pressure on the output of Chromel-



TC-8525-38

FIGURE 10 TEFLON CELL GEOMETRY

Alumel thermocouples is negligible, equivalent to an error of less than 1° C, up to pressures of 30 kbar. On the time scale of interest in the present experiments (time to explosion of 1 sec or more), the temperature difference between sample and the thermocouple junction should not exceed about 1° C. We have found no evidence of emf induced in the thermocouple by coupling with ac heating current. We therefore believe that the present apparatus permits measurement of sample temperature with an accuracy of 1° C.

For these experiments, the thermocouple cold junctions were maintained at the ice point, and the thermocouple output was monitored by a Varian model G-11A millivolt recorder. Power output to the heater was controlled manually by a variable transformer connected to the primary of a 12-volt filament transformer. A Leeds and Northrup model 8693 potentiometer was used to calibrate the Varian recorder immediately prior to and immediately following each experimental run.

In a typical run, the Teflon capsule was first pressurized to the desired level, e.g. 10 kbar. In the first several experiments, the temperature was controlled manually, and an initial current of about 8 amp was passed through the heater. When the sample temperature, as indicated by the millivolt recorder, reached the desired level, the heater current was reduced to a level (generally 3 to 4 amp) sufficient to maintain temperature. The temperature was maintained within a fairly narrow range, $\pm 3^{\circ}\text{C}$ by appropriate adjustments of the variable transformer. An abrupt off-scale excursion of the recorder pen marked the time of explosion. The sound of the explosion was well muffled by the pressure vessel; one might describe the sound as roughly equivalent to the sound of a typewriter bar striking the paper.

Under manual control, it was difficult to reduce the heat-up time to less than about 20 sec (heating rate of 15°C/sec). Accordingly, a simple solid-state controller has been constructed, which permits much shorter heat-up times as well as more accurate control of the test temperature during the run. The controller is now used routinely in all of our static high pressure runs.

The pressure in the Teflon cell increased by about 5% during the heat-up. We infer from the results of Lee et al that our results would not be affected by such minor pressure variations, and we have no current plans for improvement of the pressure system.

Results

We have completed our calibrating work with NM at 10 kbar and at 1 kbar. The results are shown in Figure 11, along with those of IRL. The data from the two laboratories are in reasonable agreement, and the trend noted by Lee et al.¹⁰ of an increased rate of explosive decomposition with increase in pressure is clearly evident here over a fiftyfold change in pressure.

Our experimental capability for carrying out these static high pressure experiments has thus been established, and during the next several months we plan to try to extend the pressure range. We feel it may be possible through some relatively minor design changes in our equipment, to attain pressures in the neighborhood of 70-100 kbar. During the same period we will complete our NM work with some runs at 10 bar.

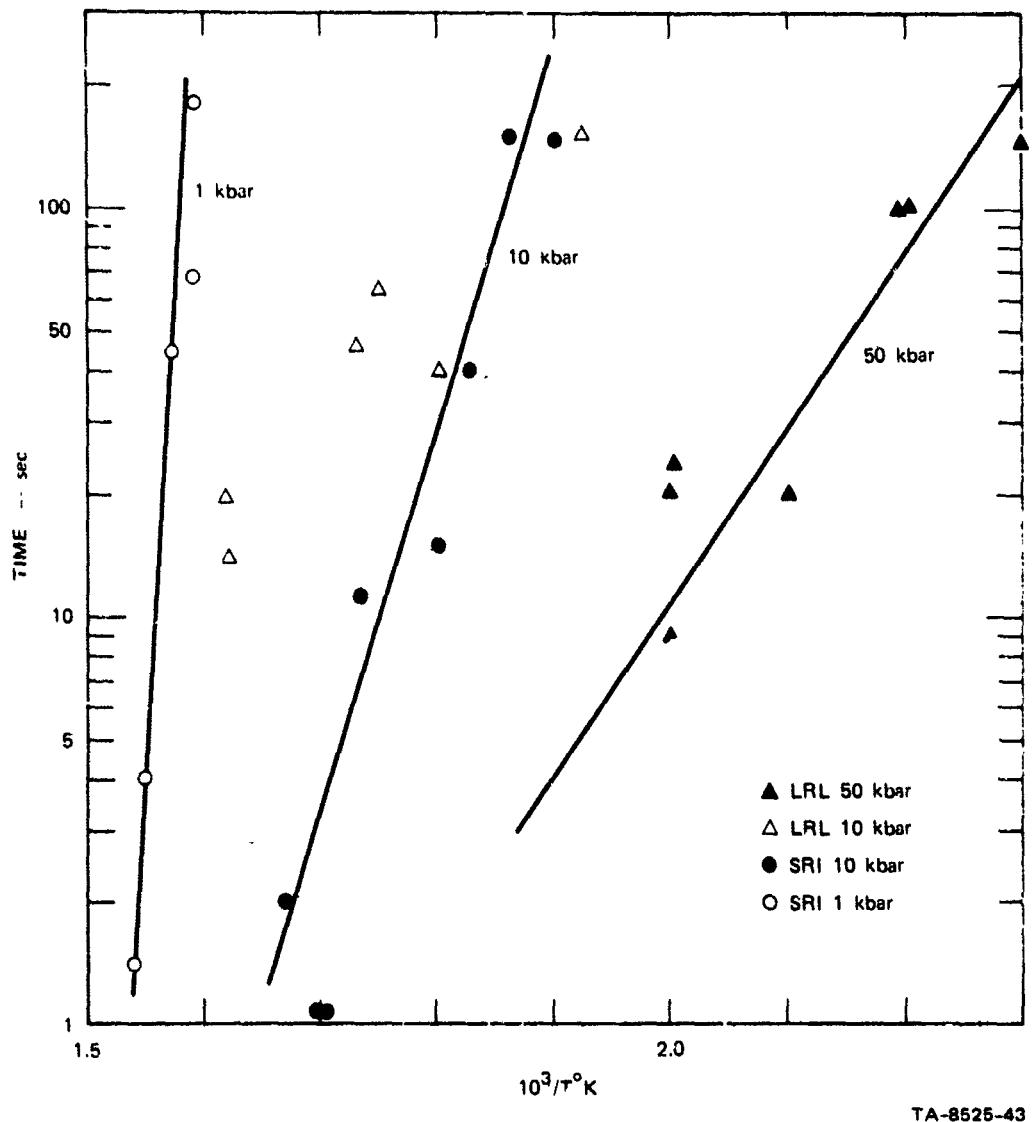
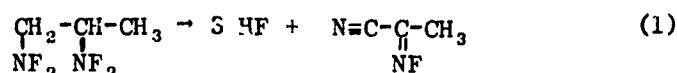


FIGURE 11 STATIC HIGH PRESSURE RESULTS FOR NITROMETHANE

D. Chemical Activation Studies

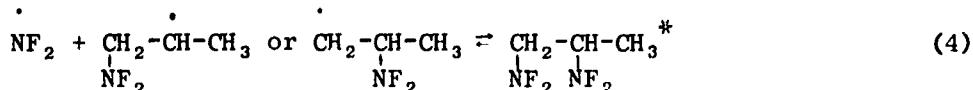
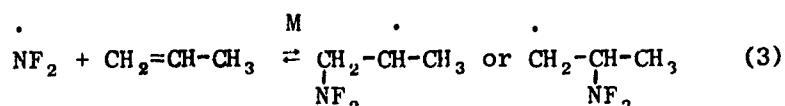
This section has been prepared in manuscript form to be submitted to to the International Journal of Chemical Kinetics.

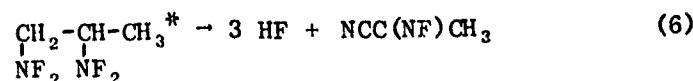
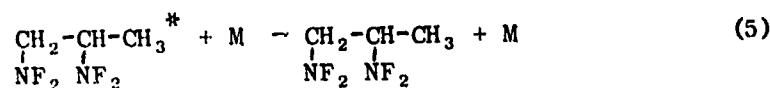
The object of this work was to determine the activation energy for the unimolecular elimination of HF from 1,2-bis(difluoramino)propane



This reaction study represents an extension of our earlier kinetic study of unimolecular HF elimination from CH_3NF_2 ($E = 42$ kcal/mole)¹³ is significant to the thermal explosion work with 1,2-DP¹⁴.

Direct observation of the HF elimination was masked by surface - catalyzed decomposition at lower temperatures, and by the competing unimolecular C-N bond scission at higher temperatures¹⁵. This problem is avoided by making vibrationally hot 1,2-DP from the successive addition of two NF_2 radicals to propylene¹⁶. The reaction sequence is then (an asterisk denotes a vibrationally excited species):





The experimental arrangement was like that used previously¹³, except that the gas chromatograph was modified to take a sample directly from the reaction vessel without having to condense the reaction mixture. No inert diluents were added and the temperature of the reaction vessel was 135°C. To confirm the retention time, some imine was prepared by the reaction of 1,2-DP with pyridine¹⁷.

By analogy with the CH_3NF_2 work, and with similar 4-center elimination reactions¹⁸ the Arrhenius factor was estimated to be $10^{13.5} \text{ sec}^{-1}$. Moreover, CH_3NF_2 was seen to go directly to HCN and 2HF, with no intermediate imine, and the same observation was made in the present case. The imino-nitrile $\text{NCC(NF)}\text{CH}_3$ was the sole organic product.

In the analogous CH_3NF_2^* system, the ratio of yield of stabilized difluoraminoalkane to the yield of HCN was observed to be a linear function of M up to 10 atmospheres pressure. In the present study, it was not possible to verify the linear effect of pressure because most of the hot 1,2-DP was stabilized even at 2 torr, the lowest pressure that could be reasonably studied.

RRK theory was used in the CH_3NF_2 work and the assumption was made that two-thirds of the oscillators were effective. The activation energy for elimination of HF was calculated to be 35 kcal/mole. When the more rigorous RRKM was used, an activation energy of 42 kcal/mole was obtained.

Since that time, Golden, Solly, and Benson¹⁹ have shown that RRKM and RRK should give the same result when the number of oscillators s is estimated from $s_T = C_{vib}^T / R = [C_p^0(T) - 8]/2$. We have estimated C_p^0 of CH_3NF_2 at 500°K to be $22 \text{ cal mole}^{-1} \text{ deg}^{-1}$ from atom additivity (we calculated from the model compounds, CH_3CH_3 , $\text{CH}_3\text{CH}_2\text{CH}_3$, CF_3CF_3 , and CH_3NH_2 that the contributions were $\text{C} = 6.2$, $\text{H} = 1.05$, $\text{N} = 5.2$, and $\text{F} = 3.8$). In this way $s_T = 7$ (compared with $s_T = 10$ obtained from the two-thirds approximation) giving an activation energy of 42 kcal/mole , in agreement with RRKM. In view of Golden, Solly, and Benson's work and the above recalculation, it was not considered worthwhile to use RRKM for the 1,2-DP experiments.

The ratio of imine to stabilized 1,2-DP at this pressure was 1 to 64. The collision frequency was taken to be $10^7 \text{ torr}^{-1} \text{ sec}^{-1}$ and every collision was assumed to have unit efficiency. The C_p of 1,2-DP at 400°K was estimated by atom additivity (simply the sum of the C_p of propylene and N_2F_4) to be $42 \text{ cal mole}^{-1} \text{ deg}^{-1}$ giving $s_T = 17$. The energy of the hot 1,2-DP was estimated to be 62 kcal/mole , based on a C-N bond strength of 59.5 and a thermal energy of 2.5 kcal/mole .

The RRK calculation gave an activation energy of 43 kcal/mole for the elimination of HF from 1,2-DP

$$\log (k/\text{sec}^{-1}) = 13.5 - 43/\theta$$

This result is not significantly different from that for elimination of HF from CH_3NF_2 .

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